



Use of oxalate sacrificial compounds to improve the photocatalytic performance of titanium dioxide

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ABSTRACT

Our study demonstrated that the performance of TiO₂ photocatalysts in eliminating organic compounds in water can be improved by combining them with calcium oxalate. The adsorption maximum capacity of Orange II on various pure photocatalysts is dependent on the specific area. Concerning the mixed TiO₂/calcium oxalate catalysts, we observed that adsorption is still higher than that of pure correspondent photocatalysts. The influence of the sacrificial agent differs according to the photocatalyst used. Thus performance of the P25-TiO₂ photocatalyst is positively slightly affected by the presence of calcium oxalate, whereas with TiO₂-PC500 a decline in photocatalytic activity can be noted. The use of calcium oxalate significantly improves the performance of titanium dioxide prepared by sol-gel. We observed similar results with the kinetics of mineralization. It seems that the effect of oxygen is the same whether pure TiO₂ samples or 70%TiO₂/30%calcium oxalate mixtures are used, regarding the rate of conversion of Orange II after 30 min of irradiation.

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1. Introduction

Photocatalytic oxidation using semi-conductors is one of the advanced oxidation processes (AOPs) for the rapid degradation of organic pollutants in water and air. TiO₂ is an excellent photocatalyst that can mineralise a large range of organic pollutants including some of the most refractory ones such as pesticides, herbicides and dyes [1–3]. The basic process of photocatalysis consists in ejecting an electron from the valence band (VB) to the conduction band (CB) of the TiO₂ semi-conductor thus creating a h⁺ hole in the valence band. This is followed by the formation of extremely reactive radicals such as •OH at the semi-conductor surface or by direct oxidation of the polluting species by h⁺. As for the ejected electrons, they react with electron acceptors such as adsorbed oxygen or dissolved in water.

However, one of the factors limiting the efficiency of photocatalysis is the rapid recombination of photogenerated electrons and holes in semi-conductor particles. Currently, many research teams are working on ways to limit the recombination of charges. Among the proposed solutions, are to be found coupling with another appropriate semi-conductor [4,5]; metal doping with

silver or gold [6,7]; adding electron acceptors such as dissolved oxygen [8] or employing organic sacrificial agents (electron donors) such as methanol [9]. For example, in order to achieve higher efficiency for photocatalytic water-splitting, many investigations in this field have made use of electron donors as sacrificial agents, which can react irreversibly with the formed oxygen or photoinduced hole to prevent the reversible reaction of H₂ and O₂ or to suppress the recombination of photoinduced electron and hole on the semiconductor surface [10].

However, in the case of the removal of organic pollutants by heterogeneous photocatalysis, the use of the soluble organic sacrificial agent gives rise to two major problems: the formation of organic intermediates and the elimination of sacrificial agent in excess.

The introduction of a solid sacrificial agent during the photocatalytic process is seldom described in the relevant literature. To our knowledge, only one publication deals with this subject [11]. Tennakone and Wijayantha [11] prepared a system where calcium oxalate is coated with paper, and on to which a layer of TiO₂ is deposited. The role of oxalate ions in the process is to consume photogenerated holes to limit their recombination with electrons. According to these authors, this system is able to extract lead from an aqueous solution under solar irradiation.

The aim of our study is to show that it is possible to improve the performance of TiO₂ photocatalysts in combination with calcium

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oxalate for the elimination of organic compounds in water. Orange II was chosen as model pollutant for comparing the performance of prepared $\text{TiO}_2/\text{Ca}(\text{COO})_2$ photocatalytic materials.

We examined the effect of the $\text{Ca}(\text{COO})_2$ concentration on two commercial TiO_2 samples (P25 from Degussa and PC500 from Millennium) and a TiO_2 synthesized by sol–gel in our laboratory. Then, we conducted the experiment in nitrogen and air in order to evaluate the influence of oxygen concentration on the photodegradation process.

2. Experimental

2.1. Reagents

All the reagents used in this work were of analytical grade and were used without any further purification: calcium oxalate (Aldrich), tetraisopropylorthotitanate $\text{Ti}(\text{OC}_3\text{H}_7)_4$ (Aldrich, 97%), ethanol (SdS-France, 99.9%), methanol (SdS-France, 99.9%) and Orange II (Sigma Chemical Co.). Titanium dioxide P25 from Degussa Corporation (70% anatase, 99.8% purity, average particle size 30 nm and specific surface of $50 \text{ m}^2/\text{g}$) and Titania PC500 from Millennium Inorganic Chemicals (anatase > 99%, surface area > 250 m^2 , crystallite mean size = 5–10 nm) were all used as supplied.

2.2. Preparation and characterization of sol–gel photocatalyst

TiO_2 was prepared by dissolving $\text{Ti}(\text{OC}_3\text{H}_7)_4$ in a methanol/ethanol solution with molar ratio 1:1:10 [12]. The resulting solution was kept at 75°C for 3 h and an appropriate quantity of water was added by drops to the hot solution (75°C). After gelling, the sample was dried at 110°C overnight and then heat-treated in air for 2 h at 450°C with a heating rate increase of $3^\circ\text{C}/\text{min}$.

Structural characterization of the prepared sample was done by powder XRD measurements, carried out with a Siemens Diffractometer Model D-5000, using a $\text{Cu K}\alpha$ radiation and operating at 40 kV and 20 Ma. X-ray diffraction spectrum (Fig. 1) shows that the resulting TiO_2 named SG- TiO_2 is pure anatase. Absorption and reflectance spectra of prepared TiO_2 were recorded by a Bruins UV–vis–NIR spectrophotometer equipped with an integrated sphere. BaSO_4 was used as a reference to measure all samples. We obtain a band gap energy value of 3.3 eV for SG- TiO_2 , close to the commercial photocatalysts (3.2 eV for P25 and 3.3 eV for PC500). The surface area measurements were performed on Coulter SA-3100 and Belsorp-mini porosimeters using N_2 as adsorbent at LN_2 temperature. BET value for SG- TiO_2 is equal to $40 \text{ m}^2/\text{g}$.

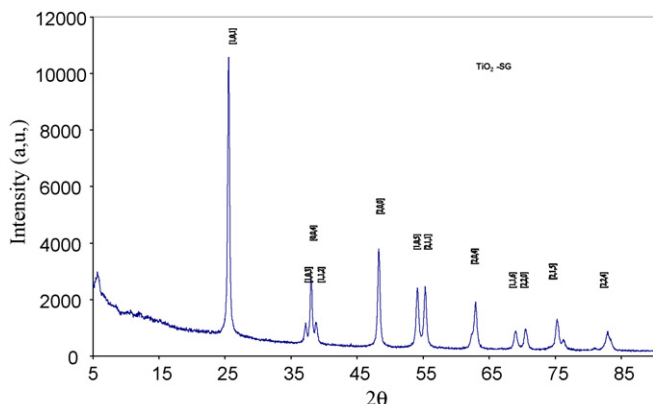


Fig. 1. X-ray diffraction patterns of the TiO_2 -SG.

2.3. Adsorption experiments

All adsorption equilibrium experiments of Orange II on the TiO_2 sample surface were carried out in batch mode under dark conditions. Studies were made using suspensions prepared by mixing a 50-ml solution of various initial concentrations of Orange II at their natural pH and TiO_2 concentration of 0.5 g l^{-1} (in deionized water). The equilibrium concentrations of Orange II in the solutions were studied after centrifugation by measuring the change in absorption intensity at this λ_{max} (484 nm) using a LIBRA S12 UV–vis spectrophotometer.

2.4. Evaluation of photocatalytic activity

Pure semiconductors (P25, PC500 and SG- TiO_2) and an appropriate weight of calcium oxalate (total weight = 50 mg) were dispersed by means of stirring in a volume of 100 ml of Orange II aqueous solution ($[\text{OII}] = 10 \text{ mg/l}$). Before each irradiation, the mixtures were sonicated for 5 min in order to disperse the catalysts, and the suspensions were kept in the dark for 1 h in order to reach the adsorption equilibrium. Irradiation was carried out with a HPK 125 W Philips mercury lamp, emitting in the wavelength range 250–600 nm, with a maximum emission at 366 nm. Between the lamp and the reactor, a circulating water Pyrex-glass tank cooler was positioned. The suspension was homogenised by a magnetic stirrer and remained in contact with air (Fig. 2). Before analysis, each sample was filtered through a $0.45\text{-}\mu\text{m}$ Whatman filter to eliminate the TiO_2 particles. During the photocatalytic test, 5 ml of the solution were extracted at given irradiation time intervals and analyzed by UV–vis spectrophotometer ($\lambda_{\text{max}} = 484 \text{ nm}$). All samples were analyzed by total organic carbon analyzer (Shimadzu TOC-5050 A) for testing the rate of photomineralization.

3. Results

3.1. Adsorption studies

Adsorption phenomena on TiO_2 are of prime importance for the photodegradation of organic molecules. The dye was strongly adsorbed onto TiO_2 materials and calcium oxalate in aqueous solution. The Langmuir isotherm model was used to describe the adsorption of OII on TiO_2 . It is given as the following equation:

$$Q = \frac{Q_m K C_e}{1 + K C_e}$$

where Q is the adsorbed amount of OII (mg/g), C_e the OII equilibrium concentration (mg/l), K the Langmuir equilibrium constant (l/mg) and Q_m the adsorption maximum capacity of OII on

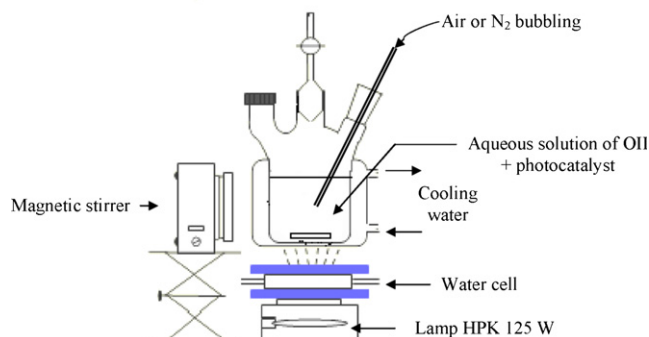


Fig. 2. Schematic diagram of experimental setup.

Table 1

Adsorption isotherm parameters of Orange II on different TiO₂ and mixed TiO₂/calcium oxalate materials

Catalysts	% of Ca(COO) ₂	Q _m (mg/g)	K (l/mg)	R ²	S _{BET} (m ² /g)
TiO ₂ -P25	0	5.780	0.248	0.996	50
	30	8.787	0.187	0.989	
TiO ₂ -PC500	0	9.328	0.126	0.991	>250
	30	10.707	0.114	0.991	
SG-TiO ₂	0	4.373	0.112	0.988	40
	30	7.559	0.180	0.995	
Without TiO ₂	100	1.967	0.450	0.999	

the TiO₂ surface (mg/g). After linearization of Eq. (1), Q_m and K can be determined by plotting C_e/Q versus C_e:

$$\frac{C_e}{Q} = \frac{1}{Q_m K} + \frac{C_e}{Q_m}$$

The Langmuir parameters for Orange II adsorbed on various titanium dioxide samples are described in Table 1.

As can be seen, the adsorption maximum capacity (Q_m) of OII on various pure photocatalysts is dependent on the specific area (see Table 1). In relation to the mixed TiO₂/calcium oxalate catalysts, we observe that the value of Q_m is still higher than that of pure correspondent photocatalysts and pure calcium oxalate. This was caused by a change in the pH solution when adding oxalate. It is well known that adsorption of Orange II on TiO₂ is highly dependent on pH and increases in acidic pH conditions [13]. The natural pH of the TiO₂/OII solutions is, respectively, 5.5, 5.3 and 5.1 for TiO₂-P25, TiO₂-PC500 and TiO₂-SG. After adding calcium oxalate, we obtained a pH of 4.3, 4.7 and 4.3 for TiO₂-P25, TiO₂-PC500 and TiO₂-SG, respectively. In addition to a small pH difference, a small adsorption difference was noted. This confirms the study of Verykios and co-workers in respect of the same dye with TiO₂-P25 [13].

3.2. Effect of calcium oxalate loading on the photocatalytic efficiency of TiO₂

We have studied the influence of the partial replacement of TiO₂ by calcium oxalate on the disappearance kinetics of Orange II under UV–vis irradiation. We increased the percentage of calcium oxalate from 0 to 50 wt.% for a total concentration of TiO₂ + calcium oxalate constant and equal to 500 mg/l. Fig. 3 shows the effect of the oxalate percentage on the photocatalytic decolourization of Orange II using three titanium dioxide samples. We can see that calcium oxalate alone is no active. In this case, the relative concentration exceeds 100% because there is a low desorption Orange II on the surface of the oxalate. The C₀ concentration at the beginning of the irradiation process is the concentration of Orange II in solution and is not adsorbed.

Fig. 3 shows that the influence of the sacrificial agent is different depending on the photocatalyst used. Indeed, the performance of the P25-TiO₂ is slightly positively affected by the presence of calcium oxalate (Fig. 3a), whereas with TiO₂-PC500 a decline in photocatalytic activity can be noted (Fig. 3b). Finally, oxalate significantly improves the performance of titanium dioxide prepared by sol–gel (TiO₂-SG, Fig. 3c). The same conclusions can be reached in relation the results of kinetic mineralization (Fig. 4). The addition of calcium oxalate improves the mineralization of Orange II in the presence of TiO₂-P25 and TiO₂-SG while this is the contrary for TiO₂-PC500.

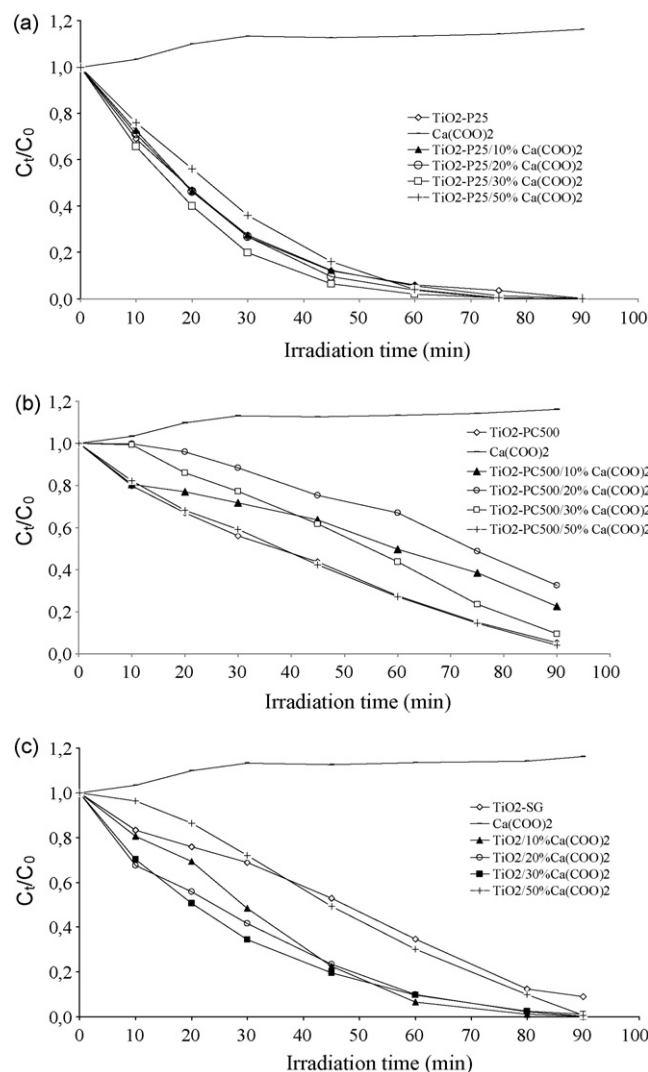


Fig. 3. Effect of calcium oxalate on the photocatalytic decolourization of Orange II ([OII] = 10 mg/l) in presence of (a) TiO₂-P25, (b) TiO₂-PC500 and (c) TiO₂-SG at natural pH.

In order to explain this phenomenon, the main characteristics and results obtained with pure photocatalysts and 70%TiO₂/30% oxalate mixtures are summarized in Table 2. It is well known that the photocatalytic degradation of Orange II is essentially an

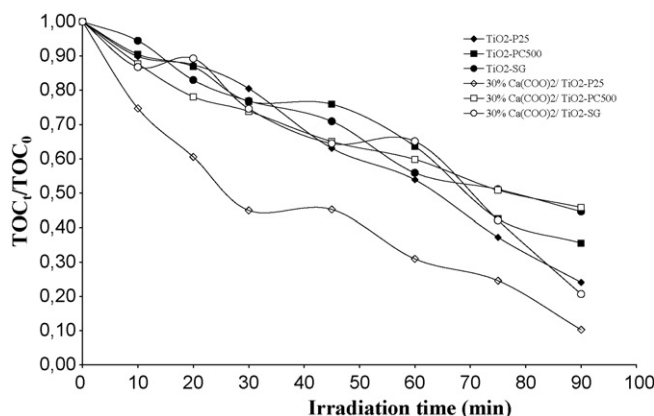


Fig. 4. Evolution of the mineralization kinetic in presence of the three kinds of photocatalysts with and without oxalate.

Table 2

Main characteristics and performance of pure photocatalysts or mixed with 30% of calcium oxalate

	Struc ^a	S _{BET} (m ² /g)	k ₁ ^b (10 ^{−3} min ^{−1})	k ₂ ^b (10 ^{−3} min ^{−1})	k ₂ /k ₁	Q _{m1} ^c (mg/g)	Q _{m2} ^c (mg/g)	Q _{m2} /Q _{m1}
TiO ₂ -P25	70A + 30R	50	46	61	1.32	5.8	8.8	1.51
TiO ₂ -PC500	100A	250	23	7.4	0.32	9.3	10.7	1.15
TiO ₂ -SG	100A	40	16	37	2.3	4.4	7.6	1.73

^a Structure: R, rutile and A, anatase.^b k₁ and k₂ are apparent rate constants for pure TiO₂ and 70%TiO₂/30% calcium oxalate, respectively.^c Q_{m1} and Q_{m2} are maximum capacity adsorption for TiO₂ and 70%TiO₂/30% calcium oxalate, respectively.

apparent first order reaction and the apparent rate constants k_{ap} , can be determined by the simplified following equation:

$$\ln\left(\frac{C_0}{C}\right) = k_{ap}t$$

We observed that TiO₂-P25 is more efficient than PC500 and TiO₂-SG in the same working conditions. Madani et al. [14] explained this difference in reactivity by reference to a better light absorption by P25 than other TiO₂. The positive effect of calcium oxalate (30%) is notable for the TiO₂-P25 (the rate constant increases by 32%) and especially for TiO₂ prepared by the sol–gel route. There the rate constant of photodegradation is multiplied by 2.3. According to Table 2, it appears that the increase in the photocatalytic activity is directly related to increased adsorption maximum capacity (Q_m) of OII at photocatalyst surface for TiO₂-P25 and TiO₂-SG. For TiO₂-PC500, the value of Q_m varies little for the 70% TiO₂/30% calcium oxalate mixture.

3.3. Effect of the presence of O₂ and N₂ during the photodegradation

Photodegradation under a bubbling of N₂ or O₂ (air) gas was also conducted throughout the reaction time, in order to investigate the possible influence of dissolved O₂ on photocatalysis. The bubbling of N₂ and O₂ gases may eliminate and increase the dissolved O₂. Figs. 5 and 6 represent the photodegradation kinetics of Orange II under a bubbling of O₂ (air) and N₂ gases for the three pure TiO₂ samples (Fig. 5) and for the 70% TiO₂/30% calcium oxalate mixtures (Fig. 6).

We can see that in all cases the deoxygenating with N₂ leads to a significant reduction of the degradation rate of Orange II, while oxygenation (with air) of the solution causes an increase in the kinetics of disappearance. According to Figs. 2 and 3, it seems that the effect of oxygen is no different between pure TiO₂ samples and 70%TiO₂/30%calcium oxalate mixtures on the conversion rate of Orange II after 30 min of irradiation.

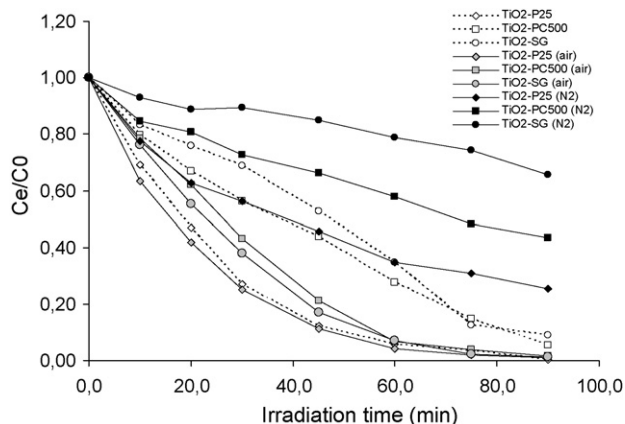


Fig. 5. Disappearance kinetics of Orange II under a bubbling of O₂ (air) and N₂ gases in presence of pure TiO₂.

4. Discussion and mechanistic consideration

The photocatalytic degradation mechanism of Orange II in presence of TiO₂ is very well described by Styliadi et al. [15]. Two mechanisms depend on light wavelength. Firstly, concerning the $\lambda < 400$ nm wavelength, the basic photocatalytic process consists in ejecting an electron from the valence band (VB) to the conduction band (CB) of the TiO₂ semiconductor, creating a “h⁺” hole in the valence band. This is due to UV irradiation of TiO₂ with an energy equal or superior to the band gap (>3.2 eV) (Eq. (1)). This is followed by the formation of extremely reactive radicals (like •OH) at the semi-conductor surface and/or a direct oxidation of the polluting species (R) (Eqs. (2)–(4)):



The ejected electrons react with electron acceptors such as oxygen adsorbed or dissolved in water (Eq. (5)):



Also, the electrons and holes may recombine together without electron donors or acceptors (Eq. (6)):



As at $\lambda > 400$ nm, TiO₂ is inactive and the degradation of OII should be explained by the sensitization of the dye by visible light photons. To summarize, when the dye is excited by visible light there is major formation of singlet excited state Orange II (¹OII*) (Eq. (7)) [16]. Then, an electron can be injected from the excited state of the adsorbed dye to the conduction band of TiO₂ (Eq. (8)), and the ejected electron can be scavenged by molecular oxygen to

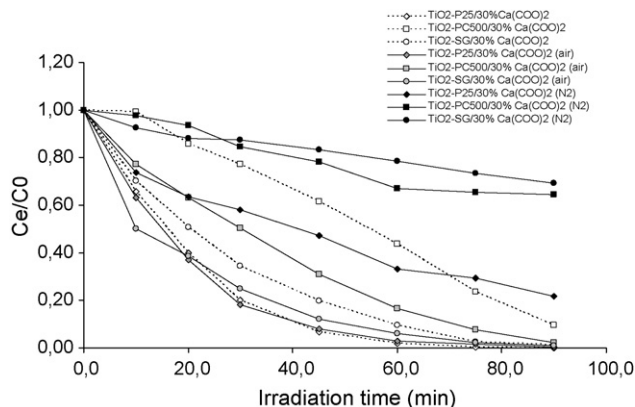
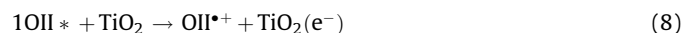
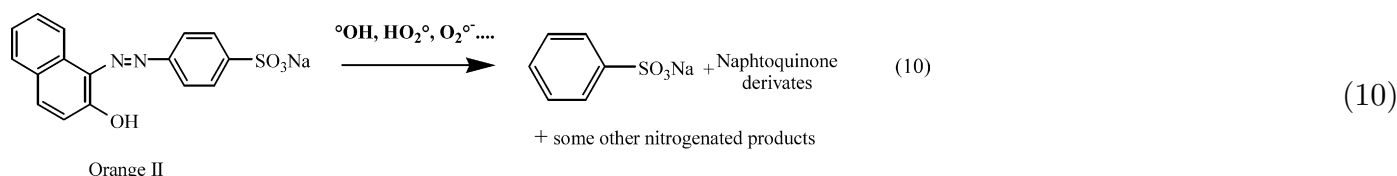


Fig. 6. Disappearance kinetics of Orange II under a bubbling of O₂ (air) and N₂ gases in presence of TiO₂/calcium oxalate mixture.

generate the superoxide radical species (Eq. (9)), which can then form other oxidative intermediate species ($\cdot\text{OH}$, $\text{HO}_2\cdot$...).



According to Styliidi et al. [15], the first step of Orange II degradation is the cleavage of the very active azo bond ($-\text{N}=\text{N}-$) which is more liable to oxidation by oxidative species with formation of benzene sulfonate and napthoquinone derivatives (Eq. (10)).

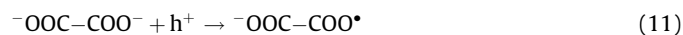


After the cleavage of the azo bond, there is a sequence of different reactions leading to total mineralization with formation of CO_2 , NH_4^+ , NO_3^- , NO_2^- and SO_4^{2-} as final products.

4.1. Calcium oxalate effect

The influence of calcium oxalate on the photocatalytic properties of titanium dioxide is difficult to explain. In addition, it is not the same for the three types of TiO_2 studied. One of the effects of $\text{Ca}(\text{COO})_2$ is to promote the adsorption of Orange II on the catalyst surface by lowering the pH of the solution.

On the other hand, calcium oxalate is oxidised by reaction with a valence band hole giving rise to a radical oxalate (Eq. (11)) and to yield carbon dioxide and $\text{CO}_2^{\cdot-}$ radical (Eq. (12)) [17].



$\text{CO}_2^{\cdot-}$ and oxalate radicals react with molecular oxygen yielding $\text{O}_2^{\cdot-}$, where $\text{O}_2^{\cdot-}$ is in equilibrium with $\text{HO}_2\cdot$ ($\text{pK}_a = 4.8$ [17]). Superoxide and hydroperoxyl radicals ($\text{O}_2^{\cdot-}/\text{HO}_2\cdot$) are key intermediates because of their strong oxidizing power, which degrades Orange II compound (Eq. (10)).

4.2. Effect of bubbling N_2 and O_2

As we can see in Figs. 2 and 3, N_2 showed great inhibitive effect on the photodecolorization of Orange II in all cases, because when the solution is deaerated by nitrogen, dissolved oxygen concentration decreases. We note that this decreasing effect is more significant in the presence of oxalate calcium. This can be explained by the absence of superoxide radicals formation by reaction between oxalate and carbonate radicals with adsorbed oxygen.

No effect of oxygen on the efficiency of P25 photocatalyst (with or without oxalate) is observed, probably because the surface of the catalyst is already saturated with oxygen. It is well known that the effectiveness of the photocatalytic reaction increases with O_2 concentration in order to achieve an optimum. In the case of other TiO_2 samples (PC500 and SG), this optimum is not reached and the introduction of oxygen can effectively increase the discoloration of

the Orange II solution, by limitation of the electron/holes recombination. The more significant effect is observed for the PC500 sample, which has a larger surface area which increases the adsorbed oxygen concentration.

5. Conclusion

In this study, we showed that in certain cases, it was possible to improve the performance of TiO_2 photocatalysts in combination with calcium oxalate for the elimination of organic compounds in water. However, the effect of oxalate was different according the kind of titanium dioxide samples employed. Indeed, the performance of the P25- TiO_2 for the degradation of Orange II is slightly

positively affected by the presence of calcium oxalate, whereas with TiO_2 -PC500 a decline in photocatalytic activity can be noted. Finally, oxalate significantly improves the performance of titanium dioxide prepared by sol-gel. The same conclusions can be reached with the results of kinetic mineralization.

Regarding the influence of oxygen concentration, in all cases deoxygenating with N_2 leads of a significant reduction to the degradation rate of Orange II, while oxygenation (with air) of the solution causes an increase in kinetics of disappearance. The effect of oxygen is no different between pure TiO_2 samples and 70% TiO_2 /30%calcium oxalate mixtures on the conversion rate of Orange II after 30 min of irradiation.

The role of this sacrificial agent is not very clear but it probably improves the photocatalytic activity on two ways:

- Increasing adsorption of Orange II on the catalyst surface by lowering the pH of the solution.
- Increasing the concentration of superoxide and hydroperoxyl radicals ($\text{O}_2^{\cdot-}/\text{HO}_2\cdot$).

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